LAMINAR BOUNDARY LAYER IN A MULTICOMPONENT MIXTURE OF GASES

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ABSTRACT

A solution is presented for the equations of laminar mul-   /25*

ticomponent boundary layer in the neighborhood of the critical

point associated with a blunt body in a flow of dissociating air.

It is assumed that the chemical reactions inside the boundary

layer are frozen. It is further assumed that the gas state

at the wall and at the external boundary layer is in equili-

brium. Two different methods are used to compute the transport

coefficients for the atomic components. The results obtained

in this fashion are compared with each other and with the sim-

plified representation of air as a binary mixture.

In considering the processes associated with dissociation

chemical reactions, mass transfer, etc., it becomes necessary

to investigate the boundary layer which contains components

with different physical properties. It is not difficult to

establish with the required degree of accuracy, the viscosity

and heat conductivity of such a mixture if we know the correspond-

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* The numbers in the margin indicate the pagination in the original foreign text.

ing properties of the individual components. It is considerably more difficult to take into account the process of diffusion in a multicomponent mixture.

At the present time wide use is made of simplifications which represent the multicomponent mixture as a binary mixture. As an example of this, we can cite the work of Fay and Riddell (ref. 1) who considered the boundary layer at the critical point of the body in a flow of dissociating air. Making use of the fact that the properties of oxygen and nitrogen are close, Fay and Riddell represented the air as a binary atomic-molecular mixture. Viscosity was established taking into account the temperature while the Prandtl number P and the Lewis number L were assumed to be constant across the layer and their values were assigned in advance.

However, we should point out that in approximating the multi-component mixture by a binary one, it is impossible in principle to take into account the process of diffusion correctly, since in this case the mutual diffusion of components whose properties are close is not taken into account. At the same time, the diffu-sion of dissimilar components is taken into account improperly.

In the present article an effort is made to take into account diffusion in a multicomponent mixture of gases when considering heat transfer and also to consider certain special problems dis-sociated with diffusion such as the question of the similarity of concentration and enthalpy profiles.

The calculation of the frozen boundary layer in a multicom-

ponent mixture of gases is of interest. In this case, diffu-
sion produces a maximum effect on the flow in the boundary layer
since it determines, to a large extent, the profile of concen-
trations.

1. Basic Equations. Let us consider the laminar boundary layer at the
frontal critical point of a blunt axisymmetrical body in a high temperature
flow of dissociating air. We shall assume that the air consists of five com-
ponents: atoms and molecules of oxygen and nitrogen as well as nitrogen oxide.
We shall assume that the rate of chemical reactions inside the boundary layers
is negligibly small and that on the surface of the body the rates are infinitely
high; as a result of this, there is thermodynamic equilibrium at the wall. We
shall assume that the gas is also in a state of equilibrium at the external
boundary of the boundary layer. We neglect thermal diffusion.

With these assumptions the system of differential equations for the boundary
layer will assume the following form (infinitesimal decimals of the second order
are not considered):

Continuity equation

$$\frac{1}{jx}(\rho r) + \frac{\partial}{\partial y}(\rho v y) = 0$$

(1.1)

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Conservation of momentum equation

$$\rho u \frac{\partial u}{\partial x} + \rho v \frac{\partial u}{\partial y} = -\frac{dp}{dx} + \frac{\partial}{\partial y}\left(\mu \frac{\partial u}{\partial y}\right)$$

(1.2)

Energy equation

$$\rho u c_p \frac{\partial T}{\partial x} + \rho v c_p \frac{\partial T}{\partial y} = \frac{\partial}{\partial y}\left(\lambda \frac{\partial T}{\partial y}\right) + \sum \rho c_i c_{1i} V_i \frac{\partial T}{\partial y}$$

(1.3)

Continuity equation for each component

$$\rho u \frac{\partial c_i}{\partial x} + \rho v \frac{\partial c_i}{\partial y} = \frac{\partial}{\partial y}(\rho c_i V_i) \qquad (i = O, N, O_2, N_2, NO)$$

(1.4)

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Boundary conditions:

$$u = v = 0, \quad T = T_w, \quad c_i = c_{iw} \quad \text{when } y = 0 \quad \textit{(at wall)}$$

$$u \to u_e, \quad T \to T_e, \quad c_i \to c_{ie} \quad \text{when } y \to \infty \quad \textit{(at external boundary of boundary layer)}$$

Here x and y are coordinates directed along the surface of the body and normal to it; u and v are the velocity components along these coordinates; r is the distance from the axis of symmetry of the body; V_i is the diffusion velocity of the i-th component; ρ, T, μ, c_p, and λ are respectively the density, the temperature, viscosity, specific heat and the heat conductivity of the gas; p is the pressure, c_i is the gravimetric concentration of the i-th component.

The subscript w designates the values of the parameters at the wall, while the subscript e designates their value at the external boundary of the boundary layer.

2. Transport Coefficients and the Termodynamic Properties of the Gas Mixture.

An examination of the diffusion process described in the monograph of Hirschfelder, Curtiss and Byrd (ref. 2) has shown that the diffusion rate in a multicomponent mixture of gases depends both on the concentration and on the gradients of concentrations for individual components.

$$V_i = \frac{M_i}{M c_i} \sum_j D_{ij} \frac{\partial c_j}{\partial y} \tag{2.1}$$

where M_i and M are the molecular weights of the i-th component and of the mixture.

The quantities D_{ij}, called the coefficients of diffusion of a multicomponent mixture represent rather complex functions of the binary diffusion coefficients of all considered components D_{ij} and their concentrations. The difficul-

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ties associated with utilizing equations (2.1) for the diffusion rate increase very rapidly with the number of components. Therefore in considering a mixture with five components, it was decided to utilize the approximation formula for the diffusion law proposed by Wilke (ref. 3). According to Wilke, the diffusion rate is given by the expression

$$V_i = \frac{1}{c_i} D_i \frac{\partial c_i}{\partial y} \tag{2.2}$$

and the proportionality factors D_i depend only on the concentrations of individual components and on the coefficients of binary diffusion

$$D_i = (1 - x_i) / \sum_{j \neq 1} \frac{x_j}{D_{ij}} \tag{2.3}$$

where   are the molecular concentrations.

To compute the coefficient of dynamic viscosity of a multicomponent mixture from the viscosity of individual components, the Mann formula was used (ref. 4).

$$\mu = \left(\sum \frac{c_i}{\mu_i} \right)^{-1} \tag{2.4}$$

The coefficients of heat conductivity of the mixture are determined by means of a formula considered in ref. 5.

$$\lambda = 0.5 \left[\sum x_i \lambda_i + \left(\sum \frac{x_i}{\lambda_i} \right)^{-1} \right] \tag{2.5}$$

In spite of their simplicity, relationships (2.4) and (2.5) give results which are in good agreement with those obtained from more complex formulas and from direct measurements.

Let us now describe the method of computing the properties of individual components. To compute the viscosity coefficients and the binary diffusion coefficients we used relationships proposed in ref. 2.

$$\mu_i = 2.724 \cdot 10^{-7} \frac{(1/T)^{0.5}}{\sigma_i^2 \Omega_V} \qquad \left[\frac{kg \cdot sec}{m^2} \right] \tag{2.6}$$

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$$D_{ij} = 1.858 \cdot 10^{-7} \frac{T^{1.5}[(M_i + M_j)/M_i M_j]^{0.5}}{p[(\sigma_i + \sigma_j)/2]^2 \Omega_D} \left[\frac{M^2}{sec}\right] \tag{2.7}$$

The collision integrals Ω_V and Ω_D which enter into these expressions were determined under the assumption that the forces of intermolecular interaction are described by the Lennard-Jones potential.

For convenience, the collision integrals were approximated by the exponential expressions

$$\Omega_V = 1.157 \, (Tk/\varepsilon)^{-0.1472}$$
$$\Omega_D = 1.074 \, (Tk/\varepsilon)^{-0.1604} \tag{2.8}$$

In the relative temperature variation range $10 \leqslant Tk/\varepsilon \leqslant 100$, the accuracy of expressions (2.8) for Ω_V and Ω_D is, respectively, 0.15% and 0.5%. For relationships (2.8) produce an error which reaches a magnitude of 5.5%.

The parameters of the potential function for the interaction between particles σ and ε which enter into the above expressions are known with a sufficient degree of accuracy only for the individual molecules and atoms of inert gases. In the case of oxygen and nitrogen atoms, these parameters have not been computed to date because theoretical calculations associated with the incomplete outer electron shells of these atoms are rather difficult. It is also not possible to obtain these values experimentally by measuring viscosity or diffusion.

Therefore in computing the properties of atomic components, two different methods were used.

Method 1. At a temperature of 2500°K the viscosity of atomic components and the coefficients of binary diffusion of atoms with atoms and atoms with molecules were determined by using a model of rigid spheres. The results which were obtained were extended over the entire range of temperature variations

by means of the following expressions

$$\mu_i = a_i T^{0.6472}, \qquad D_{ij} = b_{ij} T^{1.6604}/p \qquad (a_i, \ b_{ij} = const) \tag{2.9}$$

The corresponding properties of the molecular components were computed on the basis of the Lennard-Jones potential by means of equations (2.6) and (2.7), which assumed the form (2.9) after they were substituted into expressions (2.8) for the collision integrals.

Method 2. The properties of all components were computed on the basis of the Lennard-Jones potential. In this case the values of constant σ for atoms (the distance between atoms for which the interaction energy is equal to zero were taken from (ref. 6), while the quantities   were determined from existing data for inert gases by interpolation over the atomic weights. This procedure is not legitimate since the difference in the structure of the outer electron shell of inert gases and atoms of oxygen and nitrogen leads to a substantial difference in the nature of interaction. Nevertheless, in view of the fact that at the present time there is no satisfactory method of computing the kinetic coefficients for dissociating gases, it is interesting to follow the effect of the method of computing these coefficients on the solution of boundary layer equations.

ε/k

$3 \leqslant Tk /\varepsilon \leqslant 10$

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We present the values of the parameters for the potential function of interaction between particles which were used in the calculations

Component	O	N	O_2	N_2	NO	
$\sigma_i =$	2.96	2.88	3.433	3.681	3.47	[Å]
$\varepsilon_i/k =$	44	38	113.2	91.47	119	[°K]

The values of the coefficients a_i in equation (2.9) for the coefficients of viscosity   computed by both methods were as follows:

Component. | O | N | O₂ | N₂ | NO

$$a_i \cdot 10^7 = \quad 0.400 \quad 0.380 \quad 0.545 \quad 0.459 \quad 0.505 \quad \text{(Method 1)}$$
$$a_i \cdot 10^7 = \quad 0.628 \quad 0.608 \quad 0.545 \quad 0.459 \quad 0.505 \quad \text{(Method 2)}$$

Similar calculations for the coefficient b_{ij} in equation (2.9) for binary diffusion produced the following values:

Components   O=N   O—O₂   O—N₂   O—NO   N—O₂

$$b_{ij} \cdot 10^8 = \quad 0.2276 \quad 0.1587 \quad 0.1508 \quad 0.1585 \quad 0. \blacksquare \quad \text{(Method 1)}$$
$$b_{ij} \cdot 10^8 = \quad 0.410 \quad 0.2615 \quad 0.253 \quad 0.260 \quad 0.\blacksquare \quad \text{(Method 2)}$$

Components   N=N   N—NO   O₂—N₂   O₂—NO   N₂—NO

$$b_{ij} \cdot 10^8 = \quad 0.1605 \quad 0.1745 \quad 0.168 \quad 0.1716 \quad 0.1688 \quad \text{(Method 1)}$$
$$b_{ij} \cdot 10^8 = \quad 0.2725 \quad 0.283 \quad 0.168 \quad 0.1716 \quad 0.1688 \quad \text{(Method 2)}$$

Figure 1 shows the results of computing the viscosity of air μ at a pressure of 10 atmospheres and at temperatures up to 6000°K according to data published by E. N. I. N. (ref. 7) - curve 1; by methods 1 and 2 of the present work - curves 2 and 3, respectively; curve 4 is constructed from the well known equation of Southerland.

The coefficients of heat conductivity for individual components were determined by taking into account the Eiken correction for the energy transfer associated with the vibratory and rotational degrees of freedom in polyatomic molecules.

$$\lambda_i = 0.857 \, \mu_i \left(\frac{1}{M_i} + 1.55 c_{pi} \right) \tag{2.10}$$

The specific heat and enthalpy of the components were computed from tabulated data which were approximated by polynomials of third and fourth degree.

Above we have mentioned that the air composition at the external boundary of the boundary layer and at the surface of the body is assumed to be in equili-
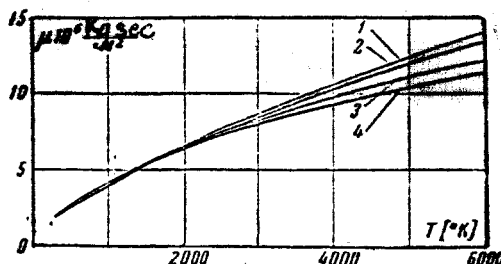

Figure 1

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brium. The equilibrium concentrations of individual components were determined from data published by E. N. I. N. (ref. 8). These data were obtained by assuming that the air contains argon. In the present work argon is neglected because the quantity of this gas contained in air was reduced to the molecular nitrogen.

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3. Transformation of the initial equations. By using the Dorodnitsyn-Stepanov transformation

$$\xi = \int_0^x \rho_w \mu_w u_0 r^2 dx, \qquad \eta = \frac{r u_e}{\sqrt{u_\xi^2}} \int_0^y \rho dy \qquad (3.1)$$

and by introducing the stream function f and the dimensionless temperature θ, the system (1.1) - (1.4), taking into account (2.2), is reduced to a system of ordinary differential equations.

$$(lf'')' + ff'' + \frac{1}{2}\left(\frac{\rho_e}{\rho} - f'^2\right) = 0 \qquad \left(l = \frac{\rho\mu}{\rho_w\mu_w}\right) \qquad (3.2)$$

$$\left(\frac{l}{Pr}\theta'\right)' + c_p f\theta' + \frac{l}{Pr}\sum c_{pi}Le_i c_i'\theta' = 0 \qquad \left(\theta = \frac{T}{T_e}\right) \qquad (3.3)$$

$$\left(\frac{l}{Pr}Le_i c_i'\right)' + f c_i' = 0 \qquad (i = O, N, O_2, N_2, NO) \quad, \qquad (3.4)$$

With boundary conditions

$$f = f' = 0, \quad \theta = \theta_w, \quad c_i = c_{iw} \text{ when } \eta = 0$$
$$f' \to 1, \quad \theta \to 1, \quad c_i \to c_{ic} \text{ when } \eta \to \infty$$

The above system was solved numerically by the method of successive approximations using the electronic computer at the Moscow State University. Since the boundary conditions were assigned at different boundaries each of equations (3.2)-(3.4) was integrated by the sweep method.

4. Modification of the Wilke equation. An independent solution of all five equations for the concentrations (3.4), utilizing the Wilke equation for

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the coefficients of diffusion (2.3), shows that in this case the identity $\Sigma c_i \equiv 1$, is not satisfied inside the boundary layer which is contrary to the physical concept.

The maximum difference Σc_i from unity is achieved when the value of η is from 1 to 2.5, and the quantity $|\Sigma c_i - 1|$ reaches a value of 0.03.

This peculiarity is not a mathematical error produced by the approximations used in the calculations. In the first place, similar calculations for the binary mixture show that $\Sigma c_i \equiv 1$. inside the entire boundary layer. In the second place the sum of concentrations for multicomponent mixture of gases does not change with an increase in the number of iterations or with a decrease in the magnitude of the integration step. This shows that the Wilke equation (2.3) which was used by us to compute the diffusion fluxes is not accurate in the case of a multicomponent mixture $(n>2)$.

Although Σc_i differs little from unity, the effect of this fact on the derivatives of the concentrations is substantial. In this case the sum of the derivatives of concentrations at the wall may have the same order of magnitude as the maximum derivatives of individual concentrations. This phenomenon has to be considered and therefore in the present work, after all the components in the boundary layer were determined independently, a correction was introduced for each concentration which was proportional to the modulus of the derivative of this concentration at the wall.

The new value of the concentration was determined by means of the expression

$$c_i^{(1)} = c_i^{(0)} + \frac{1 - \Sigma c_i^{(0)}}{\Sigma |c'_{iw}|} |c'_{iw}| \qquad , \tag{4.1}$$

This method of introducing the correction produces a proportional variation in the derivatives of all concentrations at the surface of the body.

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5. Results of the Calculations. The calculations were carried out for the following range of parameters

$$300 \leqslant T_e \leqslant 6\,000°K, \quad 300 \leqslant T_w \leqslant 3\,000°K, \quad 0.1 \leqslant p \leqslant 10 \; atmospheres.$$

The principal part of the calculations was carried out for p = 10 atmospheres.

To compare the results on heat transfer obtained in this manner with existing data for the case of a binary mixture (ref. 1), Fig. 2 shows the variation in the coefficient of heat transfer $N°$ as a function of temperature T_e at the wall temperature. Curves A were obtained by the first method of the present work, curves B were obtained by the second method, curves C were constructed from data published by Fay and Riddell with a Lewis number L = 1, curves D were constructed from the same data for L = 1.4 and curves E for L = 2; the numbers on the curves designate the wall temperature in degrees Kelvin

$$N° = \frac{N_w}{R_w{}^{0.5} \, P_w{}^{0.4} l_e{}^{0.4}} \qquad \left(l_e = \frac{\rho_e \mu_e}{\rho_w \mu_w} \right).$$

Here N is the Nusselt number, R is the Reynolds number, P is the Prandtl number, l_e is the correction factor, the subscript w is used for values at the wall, while the subscript e is used for values at the external boundary of the boundary layer.

It follows, first of all, from Figure 2 that when the temperature inside the boundary layer is below 2000°, when dissociation is practically absent, there is no constancy in the complex $N°$. This can be explained by the fact that in this method of computing the properties of air the correction factor $l_e{}^{0.4}$ does not take into account properly these properties across the boundary layer. In addition to this, the behavior of curves in Figure 2 when $T_e > 2000°$ has a disorganized nature. For example, when $T_w = 300°$ (method 2) the presented coefficient of heat transfer

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first decreases and then increases even though the numbers L_i for atoms of oxygen and nitrogen are of the order of 1.4. Furthermore, if in the computation of the properties of air according to method 2 there is a definite variation in N° as a function of wall temperature T_w, the cur T_w for method 1 frequently intersect each other.

It turned out that in the utilization of viscosity laws for taking into account the variable properties of air in the boundary layer the best results are obtained with a correction factor $l_c^{0.465}$ or $(T_w/T_e)^{0.165}$. If we now construct a variation for the complex

$$N_0 = \frac{N_w}{R_w^{0.5}\, P_{0.4}\, (T_w/T_e)^{0.165}}$$

as a function of temperature at the external boundary of the boundary layer, the picture becomes more orderly. In this connection, we should note that with an increased deviation in the number L_i for atomic components from unity, the effect of surface temperature on the reduced coefficient of heat transfer becomes more pronounced. This effect does not follow from the Fay and Riddell equation, as we can see from Fig. 2.

The presence of substantial discrepancy between the coefficients of heat transfer in the two methods of computing the kinetic coefficients of air shows that it is necessary to compute these properties more accurately.
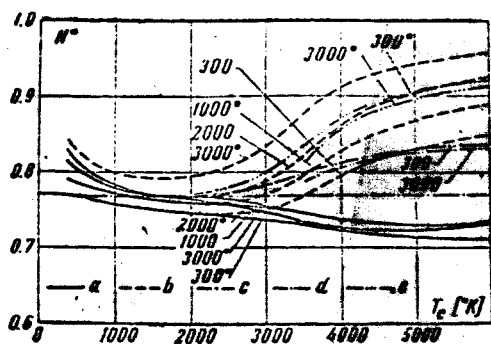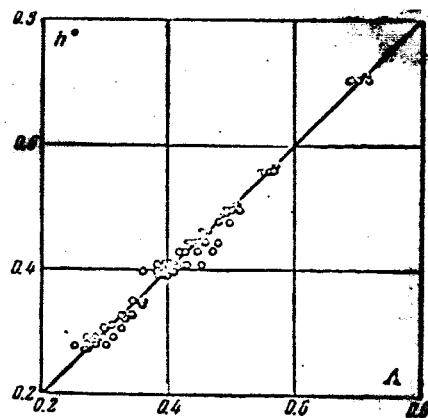

Figure 2.

Figure 3

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In developing approximation methods for computing the boundary layer it is frequently proposed that the profiles of enthalpy and concentrations are similar (ref. 9). Generally speaking, this is true only in the case when $L_i = P = 1$. Sometimes a modified analogy between diffusion and heat exchange is considered which takes into account the fact that the numbers L_i and P are different from unity. Thus for a triple mixture in the case when gas is blown in through the surface of the body, A. B. Karasev (ref. 10) obtained the following equation which relates the derivatives of enthalpy and of concentrations at the wall

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$$\frac{c_{iw}'}{c_{ie}-c_{iw}} = \frac{2.27}{P^{0.5}L_i}\, \frac{T_w}{T_e}\left(\frac{M_V}{M_i}\right)^{64}\frac{h_w'}{h_e-h_w},\qquad (5.1)$$

where M_V is the molecular weight of the gas which is blown in.

In regard to the last equation, we note that in this case the effect of the temperature factor is increased. Also this relationship turns out to be unsuitable for the limiting case $L_i = P = 1$.

The results of the present work show that in the range of investigated air parameters variation, the relative derivatives of enthalpy and the concentrations differ from each other by not more than 20%. In this case the basic parameter whose variation disrupts the similarity between the profiles of enthalpy and concentrations is the number L. Fig. 3 shows the variation in the relative derivative of enthalpy at the wall as a function of concentration.

$$h^e = \frac{h_w'}{h_e-h_w}\quad \text{from} \quad \Lambda = L_{iw}^{0.3}\frac{c_{iw}'}{c_{ie}-c_{iw}}$$

It follows from this figure (the dark points were obtained by the first method while the light points were obtained by the second method) that the following relationship is satisfied with an accuracy of $\pm$ 10%:

$$L_{iw}^{0.3}\frac{c_{iw}'}{c_{ie}-c_{iw}} = \frac{h_w'}{h_e-h_w}.\qquad (5.2)$$

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It is interesting to note that in the case when the Lewis numbers L_i for all of the components are close to unity (method 1), the analogy between diffusion and heat exchange takes place with a high degree of accuracy even though the number P varies substantially from unit $(P \approx 0.7)$.

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